SIMULTANEOUS DETERMINATION OF ARSENIC (III) AND ARSENIC (V) IN POLLUTED SG. RUI, PERAK WATER SAMPLES

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UNIVERSITI SAINS MALAYSIA

2020

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by

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Thesis submitted in partial fulfilment of the requirements
for the degree of
Master of Science (Forensic Science)

September 2020

CERTIFICATE

This is to certify that the dissertation entitle Simultaneous Determination of Arsenic (III) and Arsenic (V) in Sungai Rui, Perak Samples is the bona fide record of research work done by Ms Alradhiatul Zulaikha Binti Mohd Aljaffry during the period from February 2020 to September 2020 under my supervision. I have read this dissertation and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Master of Science (Forensic Science).

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DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except where otherwise stated and duly acknowledge. I also declare that it has not been previously for concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research and promotional purposes.

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(ALRADHIATUL ZULAIKHA BINTI MOHD ALJAFFRY)

Date: 9/9/2020

ACKNOWLEDGEMENT

The master research had been very tough and challenging task. Firstly, Alhamdulilah, I have successfully completed this research despite there is pandemic Covid-19 outbreak in Malaysia. Thanks to Allah the most gracious and merciful. A very big thanks to my supervisor, Dr Nurasmat Binti Mohd Shukri for her help, support, advice and motivation along this journey. My appreciation also goes to my supportive friends especially to Wan Nur ‘Afifa Binti Wan Mustapa for her motivations and to course mates who contribute upon completion of my projects.

My recognition and thanks also awarded to all Forensic lab assistants for their guidance and advice during the lab session. Lastly, my gratefulness and affection goes to my parents who give priceless support and motivation to me during completion of my project. I am thankful to made this far but nothing was possible. Thank you so much for the contributions.

TABLE OF CONTENT

LIST OF TABLE

LIST OF FIGURE

LIST OF SYMBOL AND ABBREVIATION

µg/kg	microgram per kilogram
AAS	Atomic Absorption Spectrometry
Ag/AgCl	silver / silver chloride
As	Arsenic
As_2O_3	Arsenic Trioxide
As^{3+}	Arsenite
As^{5+}	Arsenate
As(III)	Arsenic (III)
As(V)	Arsenic (V)
AsH_3	Arsine
$AsHO_4Pb$	Lead Arsenate
AsO_5	Arsenic Pentoxide
ASV	Anodic Stripping Voltammetry
ATSDR	Agency for Toxic Substance and Disease Registry
Au	Gold
Au-PtNPs	Gold-Platinum Nanoparticles
$Ca_3(AsO_4)_2$	Calcium Arsenate
CCA	Chromate Copper Arsenate
CCME	Canadian Council Minister of Environment
CMP	Chemical Mechanical Polishing
CS	Cathodic Stripping
CSV	Cathodic Stripping Voltammetry
Cu	Copper
Cu(II)	Copper (II)
CV	Cyclic Voltammetry
CVD	Chemical Vapor Deposition
DPV	Differential Pulse Voltammetry
DPASV	Differential Pulse Anodic Stripping Voltammetry
EGS	Environmental Goods and Service Information

EPA	Environmental Protection Agency
Fe	Iron
GC	Gas Chromatography
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICP-MS	Inductive Coupled Plasma – Mass Spectrometry
KCl	Potassium Chloride
LEDs	Light emitting Diodes
mg/kg	milligram per kilogram
mV	milivolt
$NaAsO_2$	Sodium Arsenite
NaOH	Sodium hydroxide
Ni	Nickel
Pb	Lead
ppb	Part per billion
S	Sulphur
SWASV	Square Wave Anodic Stripping Voltammetry
SWV	Square Wave Voltammetry
UNICEF	United Nation International Children's Emergency Fund
V	Volt
WHO	World Health Organisation

LIST OF APPENDICES

SIMULTANEOUS DETERMINATION OF ARSENIC (III) AND ARSENIC (V) IN POLLUTED SG. RUI, PERAK WATER SAMPLES

ABSTRACT

Contamination of the environment with arsenic (As) from both natural sources and anthropogenic activities has occurred in many parts of the world and also has been recognised as a global problem. Although there is no specific legislation for As species values but the researchers found that inorganic arsenic compounds are far more toxic and harmful than the organic ones. As contamination in Sungai Rui, Perak is widespread due to the mining location near the river. Objective of this research is to determine the concentration of inorganic As in polluted Sungai Rui, Perak sample. Therefore, anodic stripping voltammetry (ASV) method is preferred for As analysis mainly owning to its high selectivity and sensitivity. The highest concentration of As(V) was noticeable in STA 10 (8.420±0.408) µg/L and the lowest was in water sample labelled STA 22 (3.323±0.385) µg/L. Most of the concentration of As(V) detected in between 3-7 µg/L while for As(III) could not be established due to unsuitable condition. Thus, further study need to be done to achieve suitable method for simultaneous detection of As(III) and As(V).

PENENTUAN SERENTAK BAGI ARSENIK (III) DAN ARSENIK (V) DALAM SAMPEL AIR SG. RUI, PERAK YANG TERCEMAR

ABSTRAK

Pencemaran alam sekitar dengan kehadiran arsenik (As) dari sumber semula jadi dan aktikiti antropogenik telah berlaku di serata dunia dan masalah ini juga telah diakui sebagai masalah global. Walaupun masih tidak ada undang-undang khusus untuk menilai jumlah kehadiran As, tetapi para penyelidik mendapati bahawa sebatian As tak organik memiliki ciri-ciri toksik dan jauh lebih berbahaya berbanding As organik. Pencemaran As di Sungai Rui, Perak semakin meluas kerana mempunyai lokasi perlombongan berhampiran sungai. Objektif penyelidikan ini adalah untuk mengetahui kepekatan As tak organik dalam sampel Sg. Rui, Perak yang tercemar. Analisis As lebih sesuai menggunakan kaedah voltametri pelucutan anod (ASV) kerana kaedah ini mempunyai daya pemilihan dan kepekaan yang tinggi. Kepekatan tertinggi untuk As(V) yang dikesan dalam sampel STA 10 adalah 8.420±0.408 µg/L dan nilai yang paling rendah dalam sampel air bertanda STA 22 adalah 3.323±0.385 µg/L. Secara puratanya kepekatan As(V) yang dikesan antara 3-7 µg/L manakala untuk As(III) tidak dapat ditentukan disebabkan keadaan yang tidak sesuai justeru itu kajian lanjutan yang lebih mendalam perlu dilakukan untuk mencapai kaedah yang lebih sesuai bagi menentukan pengesanan serentak sumber As(III) dan As(V).

CHAPTER 1

INTRODUCTION

1.1 Introduction

Arsenic (As) is an element that naturally occurred, most prolific element in earth and also considered one of the most toxic elements, their primary used usually in pesticide, herbicide and sometimes it is used for preservation on wood for resistance from rotting and decay. As and its related compounds are mobile in the climate system and it is difficult to eliminate. However, the interaction of As with oxygen or other molecules that found in the air, soil and water or even with bacteria that living in the sediments may cause As to change its composition when attached to or separated from different particles (Fergusson, 1990). Since As can dissolve in water, therefore it can contaminate streams, rivers or open water by dissolving in rain or by discarding industrial wastes.

These toxic elements are highly resistant to chemical degradation and As exposure can cause a wide range of adverse health effects including cardiovascular, dermal cancer, gastrointestinal and carcinogenic effects (Nicolopoulou-Stamati *et al.,* 2016). As can be found in a combination with either in inorganic or organic substances to form many different compounds. Their toxicity, and the mobility depends significantly on its oxidation state, where the arsenite (As^{3+}) and arsenate (As^{5+}) are the predominant arsenic species that largely dependent on the environmental redox reaction (Cornelis *et al*., 2005). Usually As elements are mostly to be found in its inorganic form, namely oxyanions of trivalent arsenite ion (As^{3+}) and pentavalent arsenate ion (As^{5+}) where it is toxic and carcinogenic when in contact with living organisms (Xiao *et al.*, 2008). The formation of arsenite ion (As^{3+}) are formed under reducing conditions but for arsenate ion (As^{5+}) is

differ where it is in major form. Due to their reaction with human respiratory enzymes, As^{3+} is more soluble in water and fifty times more toxic than As^{5+} (Hughes *et al.,* 2011).

Determination of As usually can be performed using several techniques such as atomic absorption spectroscopy (AAS) or inductively coupled plasma-mass spectroscopy (IPC-MS) (Gettar *et al.,* 2000; Falk, 2000). These techniques incredibly useful in quantifying the concentration of inorganic As species however, the alternative of electrochemical technique such as voltammetry are much more attractive and also can discriminate the As ion species between As^{3+} and As^{5+}. Several electrochemical methods were described for the determination of As^{3+} and As^{5+} that based on the voltammetry principles. A large volume of published studies reported that stripping voltammetry one of the most sensitive electrochemical techniques (Welch, 2006), which normally used different types of electrodes (Harvey, 2000; Wei *et al.*, 2004; Borrill *et al.*, 2019). Recent methods were based on anodic stripping voltammetry (ASV) and mostly rely on the exclusively detection of inorganic As (Salaün *et al.*, 2007). Thus, this study focus on the simultaneous determination of As(III) and As(V) using DPASV method using gold electrodes.

Thus, this research aims is to simultaneously determine the level of As(III) and As(V) content in Sg. Rui polluted water sample using ASV technique with simple working gold electrode without modification due to their characteristic that suitable for determination As concentration and having stable intermetallic compound of gold-arsenic (Au-As) that can be formed during the deposition stage (Douglas, 2009). Besides, this study focuses in the development of electrochemical detection that based on the oxidation-reduction of inorganic As.

1.2 Problem Statement

Perak Education, Technology, Science and Environmental Committee chairman Dr Abdul Aziz Bari claimed Sungai Rui, Perak has been polluted with heavy metal element such as As that emitted from mining activities nearby the river which contributed to skin diseases among villagers who live near that area (New Straits Times, 2019). Long term exposure of heavy metal can lead to adverse in health effect such as can lead to impair or reduce function of the mental and central nervous system by having a direct effect on the development of neurotransmitters.

Arsenic contamination in water is a major concern public health threat worldwide (Chung *et al.*, 2014). The consequence of As exposure from food and water contaminated with ingested arsenic or inhaled polluted air that contain As content has been investigated in many countries and it is found to be associated with health effect such as vascular diseases, keratosis, hyperpigmentation and various types of cancer (Gibb *et al.*, 2011). In recent years, there was a growing interest in As exposure where according to US Agency for Toxic Substances and Disease Registry, the inhalation and dermal exposure of these elements was considered a minor route of exposure for the general population, but a major route for occupational workers (Agency for Toxic Substances and Disease Registry, 2015).

The wastewater that containing such as human waste, oils, soaps and chemicals and that has been infected by human use from any combinations of industrial, domestic and agricultural activities should be safely treated. To ensure its sustainability and to meet the needs of future generations, water treatment must be handled efficiently. Significant progress has been made recently in the governments production of efficient technologies but the challenges remain. Both inorganic and organic As are far more rapidly absorbed into the bloodstream and circulated through the human gastrointestinal tract. Arsenic has

been studied over the last few decades because As pollution considered an important environmental issues. Recently, the most significant concern regarding the risks posed by arsenic toxicity to human health through transportation of water, food distribution and global environmental pollutions.

Most of the sewage that produced by industries which are treated and discharged into the rivers thus raw surface water is polluted as a result of unnecessary and indiscriminate wastewater discharge directly from factories or households into drains and rivers with little to no treatment. This water quality deficiency significantly decreases water accessibility or, in the worst case scenario, poses a risk to public health by chemical contamination or the spread of diseases. To counter this problem, industrial effluent, developing countries, typically requires at least pre-treatment if not full treatment at the factories themselves to reduce the pollutant load before discharge into the sewer. This method is called pre-treatment or industrial wastewater treatment.

Past studies only focused on the detection of total As in water samples using AAS and ICP-MS methods in which these techniques cannot discriminate between As(III) and As(IV). Alternatively, researchers introduced the voltammetry method to simultaneously detect As(III) and As(V), however of they used a more complicated technique by modifying the electrode to obtain an accurate analysis. Therefore, this study implements simple voltammetry method without modifying the electrode for a better and accurate analysis.

1.3 Objective of the Study

General Objective:

To simultaneously determine As(III) and As(V) in Sg. Rui water sample using anodic stripping voltammetry (ASV) technique.

Specific Objectives:

1. To simultaneously detect the presence of arsenic(III) and arsenic(V) in Sg.Rui water samples.

2. To compare the concentration of Arsenic(III) and Arsenic(V) with permissible limit provided by WHO.

1.4 Significance of Study

A lot of studies and researches have been conducted on the investigation on the distribution of As in the environment since inorganic As is more toxic and dangerous to human health when expose in a long term period. Arsenic contamination may be due to ingestion of As that presence in water, food or polluted air. The current findings have shown that elevated levels of As in water especially in drinking water contributes primarily to the human As toxicity worldwide (Ratnaike, 2003; Islam *et al.*, 2011). In 2012, it was estimated that about 202 million people worldwide are exposed to arsenic concentrations in drinking water above 50 μg/L (Murcott, 2012).

In 2010, the INTERPOL Environmental Crime focusing on pollution crime forensics, which was adopted during International Conference on Environmental Crime in Lyon, recognising the use of forensics as a crucial component of successful environmental prosecutions. Ratnaile, (2003) reported the economic significance of As

toxicity includes medical expenses, loss of income and reduced crop productivity and quality due to contamination of soil and water. The existing environmental, economic and nutritional issues will be significantly complicated if knowledge were better understood about arsenic pollution in the food chain and if agricultural goods and livestock are found to be contaminated.

The contribution of this study should plays an important part in raising awareness of public to be wiser consumers by understanding the long term effect of these element on their body. Health issue should be first priority. Through determination of specific arsenite, As(III) and arsenate, As(V) and their level of toxicity from the Sg. Rui samples can ensure their quality of water at the area that believe have been contaminated with the As. By comparing their concentration with the permissible limit that have been provided by World Health Organisation (WHO) can ensure the environmental quality.

CHAPTER 2

LITERATURE REVIEW

2.1 Arsenic

2.1.1 Inorganic Arsenic

Heavy metals in the form of As and their compounds are known more toxic and harmful compare to other type of heavy metals when exposed to human health. Arsenic enters the aquatic environment from natural sources and is created and used through anthropogenic pollution resulting from human activities such as mining, glass making, smelting, pesticide and fertilizer. Although there is no specific legislation for As species values mention by World Health Organisation (WHO) but the researchers found that As inorganic compounds were far more toxic and harmful than the organic ones. According to WHO (2018), people are exposed to inorganic As by consuming polluted water, using contaminated water for food storage and food crop irrigation, manufacturing processes and cigarette smoking.

Arsenic is present in the environment in a wide variety of chemical forms and can alter its composition by microbes, changes in geochemical conditions and other environmental processes, this input are responsible for the discharge of As into the atmosphere and disperse by rain and dry runoff to the earth's surface (Cullen, W. R. and Reimer, 1989). Arsenic natural mechanisms include weathering, bioactivity and volcanic activity. The main anthropogenic production is generated from combustion by industry and agriculture of municipal solid waste, fossil fuels in coal-and oil-fired power plants, release from metal smelters, and direct use of herbicides containing arsenic. There are a variety of ways that arsenic can become introduced to the human population. The most

common is potentially arsenic consumed in potable water or food (National Research Council, 1999; Le *et al.*, 2000; US EPA, 2001).

There are several forms of As where inorganic As is more toxic compared to organic forms (Matschullat, 2000). Basically formation of organic As is the molecule that have a framework of carbon atoms that attach with the As atom. Organic As is varied and more complicated in structure but it is harmless compared to inorganic As (Zhang *et al.*, 2002). Inorganic As compound does not contain carbon atom and are generally simple molecules such as As trioxide and these compound are highly toxic and harmful when in contact with human. There are two types of inorganic As which are pentavalent As, arsenate (As^{5+}) and trivalent As, arsenite (As^{3+}). Many studies have been performed in the literature stating that As^{5+} is well absorbed through the intestine but less toxic than As^{3+}, which is more lipid soluble and absorbed through the skin.

Many inorganic As can be found in the environment, often occurring as a type of sulphide in complex minerals that contain different metals such as lead (Pb), copper (Cu), nickel (Ni), and iron (Fe). Common trivalent arsenic (As^{3+}) is an arsenic trioxide (AsO_3) and sodium arsenite ($NaAsO_2$) while for pentavalent forms are arsenic pentoxide (As_2O_5) and various type of arsenate (Ratnaike, 2003). From the mid-1800s to the mid-1900s inorganic arsenic compounds were widely used as pesticides and were used in medicine until the 1970s, primarily for treatment of leukaemia, psoriasis, and asthma. By the mid-1970s, As used move from pesticides to wood preservatives and became the main use by 1980 yet year end application of inorganic arsenic compounds in the USA has varies due to their effect after use (Nicholas *et al*., 2010).

2.2 The Occurrence of Arsenic

2.2.1 Transportation and Partitioning of As From Soil

There have been several studies in the literature reporting As interactions with oxygen or other molecules found in air, water or soil, as well as with soil or sediment-living bacteria (Figure 2.1) can cause As to change form, bind to, or separate from, different particles (Fergusson, 1990). Many common As compound can dissolve in water, thus As can contaminates the lakes, river and even ground water. According to Delaware Health and Social Services, in the United States, As is usually can be found in groundwater, particularly areas with shallow groundwater reservoirs and large quantities of soil and mineral arsenic (Herath *et al.*, 2016).

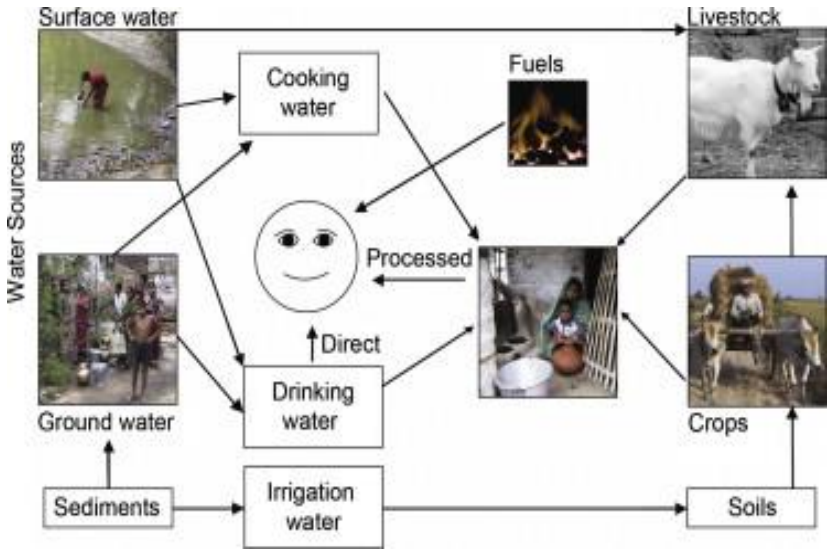

Figure 2.1: Route of Arsenic Exposure

Due to As is one of the elements that is natural part of the crust of the Earth and found most abundant in comparison with other compounds, with an average of As content varying between 2 and 3 mg/kg (Nriagu *et al.*, 2007). Inorganic As deposited into

sediments and their concentrations depending on the geological, human activities, climate changes, As formation and the conditions of the soil (De Carlo *et al.,* 2014). Interactions of water with rocks and soils that combined with deposition from the environment have triggered As exposure through air.

Interaction of As with water, rocks and soils caused from cycling of As itself under local atmospheric deposition effect. The weathering of formation geology and waste from mines results in high As concentrations (Nriagu *et al.*, 2007). The cause of mineral weathering to the environment will improve the preservation of As in soils, depending on the extent of the soil modification, weathering levels, rainfall and other environmental factors that influences the inorganic As (Cutler *et al.,* 2013; Hue, 2013). Arsenic has been studied over the latest few decades where Nickson *et al.,* (2000) observed the concentration of arsenic has closed similarities with the concentration of diagenetically of iron (Fe) and in sediments and there is no correlation could be observed between the As and sulphur (S).

To study As compound in soils is a heterogeneity in which it can occur, so that high concentration regions may be similar to region with far lower concentrations of As. Adriano (2001) and Clemente *et al* (2008) stated that in such cases, As levels are greater on surface soils horizon where it would imply that pollution occurred after the soil appears to have accumulated. However, this conditions will be depending on the source and process of As arsenic entering the soil, and altering its composition (Moreno *et al.,* 2012). Previous study by Fitz and Wenzel (2002) reported up to 1.4 million soil sites identified could be polluted with metals, metalloids and an organic compound.

By studying on how As element is distributed in soils which can provide useful information on the mobility, movement and possible toxicity of these elements. Arsenic when retained in soils within soil matrix (soil and water) it will be most mobile in term of soluble fraction and biologically active. From toxicological view, As contaminant that present in soil matrix should be used as an indicator when analysing the soils (Mench and Schwitzguébel, 2009). Mench and Schwitzguébel also reported that the availability and unavailability As pollution appears to be contained within the soil but any changes that occur in environmental factors such as pH, climate, biology, hydrology, organic matter, or alterations in mineral content for example from dissolution–precipitation, oxidation–reduction, formation of complexes–disassociation and adsorption–desorption can alter the availability of an elements that present in the soils.

2.2.2 Transportation of As Through Water

2.2.2.1 Groundwater

Soil and water are the primary sources of human As exposure at any given location, either through ingestion (González-fernández *et al.*, 2018) and according to WHO, drinking water is the main source of exposure globally of As and approximately 30 million people are estimated to be exposed to water pollution with this contaminant and many natural and anthropogenic sources are also responsible for the pollution of As in groundwater. However, by comparing the maximum level of arsenic in water provided by WHO (10 µg/L) with the concentration of arsenic in surface water, in surface water contain higher level of arsenic which are greater than 2000 µg/L in certain areas of Bangladesh and India (Tripathi *et al*., 2007).

Arsenic production is commonly mentioned in groundwater in many countries, and concentrations differ considerably depends on groundwater oxidation reduction characteristics (Bhattacharya *et al*., 2002). Arsenic contamination from different part of countries is an outcome of natural and also it may come from anthropogenic sources which have adverse effects on the human health and environment. Millions of people from different countries depend heavily on groundwater which contains high levels of As for drinking. Contamination of groundwater either from natural sources or anthropogenic activities in various regions of the globe has now become a major environmental concern such in part of Asia, the elevated As in groundwater has been documented in Vietnam, Bangladesh and State of West Bengal (Bhattacharya *et al.*, 2002; Bhattacharya *et al*., 2011).

Since groundwater is considered one of the source of drinking water, and one-third of the human population is dependent on it for ingestion thus by monitoring contamination occurrence in the groundwater level is one of the step to prevent excessing of As contamination (Emenike *et al.*, 2017). The presence of mineral and metalloids in excess of concentration in groundwater might associated with elevated of As contamination. The occurrence of As contaminant as primary constituent of over 200 mineral forms (Bissen *et al*., 2003) and the desorption dissolution of naturally occurring As bearing minerals and alluvial sediments results in excessive of arsenic in groundwater, even though As concentrations are not high in the solid phase (Matschullat, 2000; (Chakraborty *et al.*, 2015).

2.2.2.2 Wastewater

According to Garfì and Bonoli (2004), waste management in developing countries is not sustainable, relying on uncontrolled disposal in waste dumps. The effluents produce from industries such as mining, smelting and petroleum processes usually containing high As level due to their wastewater production. Its toxicity is raising environmental issues thus the limitation of discharge is applied to industrial wastewaters. For example, light emitting diodes (LEDs) manufacture, As pollutants released from industry originated from two different sources: soluble As produced from AsH_3 chemical vapor deposition (CVD) and solid residue from chemical mechanical polishing (CMP) of the end product. These type of wastewaters produced by industrials were unique in its low flow rate and containing high As concentration mostly as As^{3+} (Ahammad *et al*., 2008). Due to mining of minerals, combustion of fossil fuels, smelting, preparation of As containing drugs, volcanic eruption and the use of pesticides highly produces As in sewage (Sun *et al.*, 2019) and most countries around the world are struck hard by As contamination.

2.2.3 Transportation of As Through Anthropogenic Activities

According to Matchullat (2000) and Mandal and Suzuki (2002), anthropogenic sources of As exceeded natural sources such as through soil exposure, sedimentary exposure and volcanic eruption in the environment where 60% of anthropogenic sources are found As emissions can be accounted from the use of fertiliser application, pesticide application and smelting. Historically, As compound such as the using of calcium arsenate ($Ca_3(AsO_4)_2$), lead arsenate ($AsHO_4Pb$) and sodium arsenate have been used as pesticides and fertiliser (ASTDR, 2007). In manufacturer of glass for decolouration often use as one of their components in various metallurgical processes such as the manufacture of alloys and lead batteries (CCME, 2001; IPCS, 2001; ATSDR, 2007).

Route of As exposure that causes contamination in the general population has not been fully identified, but recently the most significant concern regarding As toxicity is thought to be transported through industrial waste, smoking, drinking water and worldwide distribution of food (Chung *et al*., 2014). All As compounds are used in industry, agriculture and medicine, and are still imported from other countries. Until 1940s, the usage of inorganic As compounds as agricultural pesticides was frequently used. Officially much of the uses of As in cultivation are prohibited in the United States. Arsenic in soil usually results from human activities, including pesticide use, mining and ore processing operations, coal burning power plants, and waste disposal operations. Past tannery sites, which produce leather from animal hides, have significant amounts of arsenic in the soil.

2.2.4 Transportation Through Industrial Effluent

There is a concurrence among the researcher that chemical industries, smelting, ore processing, mining, thermal power plants and industries related to wood preservation contribute to large volumes of As per annum to the atmosphere where estimates of global annual atmospheric emissions (Tchounwou *et al.,* 2012). Chromate copper arsenate (CCA) is one of the chemicals that being used for wood treatment caused the widened of As distribution into environments (Townsend *et al.,* 2005). CCA had reached wood preservatives industries because of the biocidal properties of Cu(II) and As(V).

As we know, heavy metals also can accumulate in the ecosystems through natural sources such as from volcano eruption, geological cycles and also from earth crust and their concentration of heavy metals specially As is associated with biological and geochemical cycles are also affected by anthropogenic activities such as shipping, waste disposal, industrialisation, social and agricultural activities have an impact on environmental degradation and the global ecosystem. These functions often have negative effect on human health and all living species. After the beginning of the industrial revolution contamination of the atmosphere with toxic metals has risen unexpectedly (Ram Proshad *et al.*, 2018).

2.3 Impact of Arsenic Exposure on Environment and Their Health Hazards

Arsenic is extremely toxic and it is one of the greatest environmental hazard which threatening thousands of people. Human being is known to consume As through environmental exposure such as from air, food and water. However, according to Chakraborty *et al.* (2015), one of the majors As exposure to people is through drinking water and being exposed to contaminated food. Arsenic exposure can cause a range of adverse effects on health, including dermal changes, respiratory problems, hyperpigmentation, mutagenic and carcinogenic effects (Mandal, B. K. and Suzuki, 2002). Even though As is a core elements but most of As compounds are toxic (Mayer *et al.*, 1993). For example, the most toxic compound is arsine gas (AsH_3) where their fatal dose is 250 mg/m^3 at an exposure time of 30 minutes (Reinhard and Kreis, 1997). While As(III) and As(V) both of their oxidation states inhibit the energizing functions of the mitochondria and can also trigger enzyme inhibition (Pontius *et al.*, 1994).

Several epidemiological studies have shown a positive association between exposure to As and increased risk of both carcinogenic and systemic health effects (Tchounwou *et al.*, 2003). Arsenic toxicity would also depend on the dosage, frequency and duration of the exposure, the biological species and human susceptibilities and nutritional factors (Tchounwou *et al*., 2004). Research also has pointed significant increases in mortality rates for lung, prostate, skin and liver cancers in many As exposure areas. These contaminants can cause acute and chronic poisoning when living things are exposed to them. Long term exposure of As through water, food and air will result in hyperpigmentation, hyperkeratosis, cardiovascular diseases and disturbance in nervous systems, circulatory disorders, eczema and suffering from liver and kidney disorder (Bertorini *et al.*, 1990; Ahsan *et al.*, 2002).

While for chronic arsenic exposure, in April 2013, Unicef stated that there is no medical cure at present for the treatment of arsenicosis. If a person has been affected in a long term of exposure of contaminant then health risks will remain for decade, even after the individual has been not being exposed at certain times. Adverse health effects of chronic exposure of arsenic often take up to twenty years to manifest (Unicef, 2013) and is often associated with various kind of health problems, such as skin disorders, diabetes, cancer and impaired cognitive development. A study by Islam *et al.* (2011), many reports indicating hyperpigmentation and skin keratosis are the two hallmark sign of arsenic exposure.

2.4 Conventional Analytical Technique for Detection of Specific Arsenic, As(III) and As(V)

2.4.1 Voltammetric Technique

For detection of As in environmental samples several methods have been introduced such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma- mass spectrometry (ICPMS), and high performance liquid chromatography with ICPMS detection but the uses of these methods for As detection presents several issues such as high cost of the instrument, less sensitive compared to electrochemical technique (Stanković *et al.*, 2020) and apparently cannot discriminate between As(III) and As(V). With the same objective, electrochemical technique like stripping voltammetry had been used to simultaneously detect various metals and semi metals with detection limits up to part per billion (ppb) concentration (Idris *et al.*, 2017). This technique deals with the study of an electrode solution interface charge transfer in terms of the analytes to gain or lose an electron that is reduced or oxidized respectively (Farrell *et al.*, 2001).

A review on the analysis and speciation of As was carried by Cavicchioli *et al.* (2004) considered voltammetry techniques for the determination of As and its speciation at trace levels in environmental, industrial and in food samples. ASV has been and continues to be one of the popular electrochemical methodologies for determination of As in water samples. As reviewed in multiple references, ASV has been developed as a leading technique in determination of inorganic trace As. In general, for inorganic As determination by ASV usually gold working electrode will be use simultaneously with the use of strong acid as supporting electrolyte.

ASV is being used to determine the concentration of trace elements because this method consists of deposition potential that is more negative than the half-wave potential of the metals to be determined and the anodic (positive going) scan to oxidize the reduce metal back into the solution (Princeton Applied Research, 2018). The analyte eventually will concentrated at the electrode surface by the application of a negative potential results, in the case of trace metals, in the electrodeposition of analytes of interest on the surface of sensor in the form of amalgam or in the form of metallic layers (Herzog and Arrigan, 2005).

2.4.2 Gold Electrode

Voltammetry development and the stripping voltammetry is closely connected with the use of mercury and few different types of electrodes such as carbon and gold. The inconvenience in working with liquid hanging drop electrode and also mercury is known very toxic and having limited range of potential for anode reactions, makes stripping voltammetry reportly not popular as it might be. Gold electrodes or modified gold electrodes are traditionally used for determination of electropositive elements such as As and few other elements. It is also known that some elements concentrated on the gold electrode very efficient due to the formation of alloys and strong intermetallics (Brainina *et al.*, 2000). The application of gold and modified gold electrode in ASV is shown in Table 2.1.

Gold has been shown to be a material of choice for electrode substrate for determination of inorganic As in ASV technique. According to Yang *et al.* (2017), the excellent electrochemical performance, such as lower of detection value and their sensitivity compare to other techniques of As detection basically was obtained at noble

metals such as Au, Pt, and Ag because of their electron transfer, large surface area and electrocatalytic ability. Besides of their interference at gold electrodes, which were formed in particular from Cu ions and organic matter in real samples, a number of methods have been developed to overcome this problem. Recently, the use of gold nanoparticles supported on carbon substrates has been shown to reduce Cu(II) ion interference and enable trace determination of As(III) (Salaün *et al.*, 2007).

Table 2. 1: Application of the different types of gold electrode in ASV method

Electrode/Substrate	Species	Sample(s)	Technique(s)	Detection limit/Concentration (µg/L)	Reference
Au-disk electrode	As (III)	Natural waters and biomaterials	DP ASV, LS ASV	0.15	(Kopanica and Novotný, 1998)
Pt wire, modified Au film	As (III), As(III + V)	Potable water	LS ASV	0.50	(Huang H *et al.*, 1999)
GC, modified with Au film	As (III)	Supporting electrolyte	LS ASV	0.50	(Brainina *et al.*, 2000)
GC, modified with Au film	As (III)	Groundwater	ASV	1.20	(Rasul *et al.*, 2002)
Au microelectrode	As (III), As(III + V)	Sea water	SW ASV SC	0.2, 0.3	(Salaün *et al.*, 2007)
GC, IGE, modified with Au film ex situ	As (III), As (V)	Mineral waters, Drinking waters, alcohol and alcohol free drinks	LS ASV	0.02	(Alghamdi, 2010)
Au nanowires	As (III), As (V)	River water	ASV	0.08	(Mardegan *et al.*, 2015)
GC, modified Au-Pt nanoparticles	As (III)	Natural waters	LS ASV	0.20	(Bu, L *et al.*, 2015)
GC, modified with Au film	As (III), As (V)	Drinking water and Natural water	ASV	0.42, 0.55	(Jedryczko *et al.*, 2016)
Au microelectrode	As (III), As (V)	Drinking water and groundwater	SW ASV	0.26, 0.39	(Zhou *et al.*, 2017)
Au electrode	As (III)	Environmental waters	ASV	0.7	(Tupiti *et al.*, 2018)

2.4.2 Cyclic Voltammetry (CV)

Cyclic voltammetry is one of the types of voltammetry where the electrochemical cell under conditions where measurement that allows to study the redox properties of a compounds and the interfacial structure (Bałczewski *et al*., 2008). Cyclic voltammetry is a widely used as electroanalytical technique which analyzes the electrochemical reactions between ions and electrode surface atoms by understanding few reactions in the cell such as intermediate reaction to obtain product reaction stability, qualitative details on electrode reaction mechanisms, qualitative charging reaction properties between electrolyte ions and electrode surface electrons (Wang, 2000). This method is often the first experiment that will be performed in an electroanalytical study because it offers a rapid location of redox reaction of the analyte of interest, and having a convenient evaluation of the effect of media during redox process. The shape of the cyclic voltammogram for reversible system is shown in Figure 2.2.

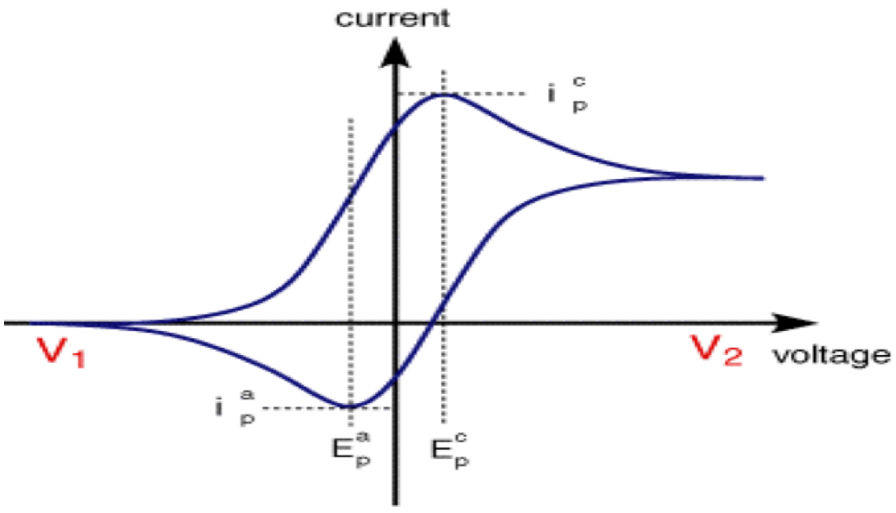

Figure 2. 2: Cyclic Voltammogram for reversible system

In Figure 2.2, the peaks are performed in both the forward and reverse scans of the CV and they are in similar shapes. If the redox system is fully reversible, their magnitudes will be identical resulting in a peak (reversible). From this CV, the direction of a scan was from a positive to a negative potential (cathodic direction) thus this direction referring to reduction occurred during forward part of the CV and the oxidation occurred during the reverse scan (Ndlovu, 2012). Since the oxidation reduction peak having the similar reaction which are reversible, hence CV will provide the information about redox potentials and electrochemical reaction rates. Single or multiple cycles can be performed for this technique.

2.4.3 Stripping Voltammetry

The term of stripping voltammetry is a form of voltammetry in which the analyte of interest is first deposited on the electrode and then removed, or stripped electrochemically during monitoring the current as a function of the applied potential (Harvey, 2000). In the past 50 years, the stripping voltammetry techniques for trace metal analysis have been known among researchers and chemists. The basic process involves the electrochemical deposition of trace metals on a suitable electrode for a few minutes and then the oxidation of metal back into the electrolyte by reversing the scanning potential, oxidation current or also known as the stripping current is reported as a function of the scan potential (Douglas, 2009).

Stripping analysis is a method that use a bulk electrolysis step to do the pre-concentration of a substance from the solution onto the electrode surface. Basically, after the electrode deposition step, the analyte of interest is "stripped off" from the electrode by using a different voltammetric techniques such as Differential Pulse Voltammetry

(DPV) and Square-Wave Voltammetry (SWV) (Lestarini and Ivandini, 2019). If the conditions during the pre-concentration step are maintained constant, to find the solution concentration can be find by measuring voltammetric response (Faulkner, 2012). The most advantage of this method is the technique is very effective in evaluating dilute solutions. This analysis is frequently used for the determination of metal ions by cathodic deposition, supported by linear-potential anodic scanning (Anodic Stripping Voltammetry, ASV) or also known as inverse voltammetry (Harvey, 2000).

2.4.3.1 Anodic Stripping Voltammetry (ASV)

Anodic stripping voltammetry is used to assess trace metal concentrations. ASV consists of a more negative deposition potential than the half-wave potential of the metals to be determined, and an anodic (positive) scan to oxidize the reduced metal back into solution. (Princeton Applied Research, 2018). The analyte is concentrated on the electrode surface by applying negative potential results for trace metals, electrodeposition of analytes of interest on the sensor surface in the form of amalgam or metallic layers (Herzog and Arrigan, 2005). Then, the detection step is performed by sweeping the electrode potential in anodic direction , resulting in the oxidation and re-dissolution of the analyte deposited at the electrode surface (Herzog and Beni, 2013). Anodic stripping voltammetry is regarded as one of the most potential and sensitive out of all methods which seemed as a promising technique to investigate for trace As determinations. Forsberg *et al.* (1975) reported that the use ASV to determine concentrations of As can be detected as low as 2×10^{-7} M.

2.4.4 Differential Pulse Voltammetry (DPV)

Since the sensitivity of detection in CV is low, the aim of DPV methods is to make it lower in their detection limits by enhancing their Faradaic currents where the electron transfers to and from an electrode. Recent advances in the instrumentation and techniques such as differential pulse anodic stripping voltammetry (DPASV) suggests that sensitivity can be increased and accuracy can be easily achieved. This technique provides improved selectivity for observing different redox processes compared to CV (Scott, 2016).

All the pulses in DPV technique are based on the sequences of the sampled current-potential steps and after the stepping potential, the charging current will decays exponentially to a negligible value while the faradaic decays slowly (Wang, 2000; Ndlovu, 2012). DPV is a system where pulses of fixed magnitude are superimposed on a linear potential slope, and this standard time excitation signal for DPV is sampled twice as the response current. Usually, the peak height from DPV technique is directly proportional to the concentration of the analyte and this peak also can be used to identify species (Hoyos-Arbeláez *et al.*, 2017).